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1.
THE STRUCTURE
OF WHITE CESIUM LEAD(II)
BROMIDE, CsPbBr_3

BY

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Synopsis

Crystals of the white modification of CsPbBr_3 —contaminated with orange crystals of the same composition—can be obtained from aqueous solutions of CsBr and PbBr_2 . The white crystals appear to be only slightly less stable than the orange ones. They are needle-shaped with γ' parallel with the needle axis and they undergo a phase transition to the orange modification at 130°C . The X-ray analysis shows that the white crystals are orthorhombic belonging to space group no. 62 Pmnb , and $a = 4.597 \text{ \AA}$, $b = 9.72 \text{ \AA}$, $c = 16.81 \text{ \AA}$. The structure is quite analogous to that of the yellow CsPbI_3 . Distorted PbBr_6 -octahedra sharing Br-atoms form chain-like, polynuclear ions $(\text{PbBr}_3^-)_n$ running parallel with the a -axis. The Pb-Br-distances vary from 2.82 \AA to 3.29 \AA .

Introduction

It has been shown previously that CsPbI_3 exists in two modifications, a black metastable form with perovskite structure and a yellow orthorhombic form which is stable under ordinary conditions¹. CsPbBr_3 apparently also exists in two forms, an orange-coloured form with perovskite structure, which already has been investigated², and the supposed analogue of the yellow orthorhombic CsPbI_3 , which has been prepared by WELLS and co-workers³.

Although a fairly complete X-ray analysis has been done on the orthorhombic CsPbI_3 , it seemed worth while to make an independent investigation of the white CsPbBr_3 in order to check the irregular octahedral coordination of the halogen atoms around the lead atoms which was found in the former compound. Also, in the previous investigation no distinction could be made between the halogen atoms and the cesium atoms because of their equal scattering powers. And finally, it might be interesting to see if the atomic parameters would be the same as in CsPbI_3 in spite of differences in absorption and dispersion effects.

Preparation and properties of the white CsPbBr_3 -crystals

We have obtained the white modification of CsPbBr_3 in the following way. First CsBr was prepared from Cs_2CO_3 and an aqueous solution of HBr . PbBr_2 was precipitated from aqueous solutions of $\text{Pb}(\text{NO}_3)_2$ and HBr , recrystallized a few times in hot water. All the chemicals were Riedel-Haën pro analysi.

Aqueous solutions with well-defined concentrations of CsBr were next prepared and saturated with PbBr_2 by boiling. Undissolved PbBr_2 was separated from the still hot solutions. On addition of an amount of hot or cold water to each solution so that the CsBr -concentrations as well as the

¹ C. K. MÖLLER, The Structure of CsPbI_3 . Mat. Fys. Medd. Dan. Vid. Selsk. **32** No. 1 (1959).

² C. K. MÖLLER, The Structure of Perovskite-like Cæsium Plumbo Trihalides. Mat. Fys. Medd. Dan. Vid. Selsk. **32** No. 2 (1959).

³ H. L. WELLS, Z. anorg. Chem. **3**, 195 (1893).

temperatures were kept within a certain range a precipitation of crystals usually resulted.

White needle-shaped crystals were obtained when the final concentration of CsBr was in the range 23.5–27.5 g CsBr/100 g H₂O, and the temperature at which they appeared was usually 23–25°C; but they were always contaminated with orange crystals, and sometimes also with thin flaky crystals (of CsPb₂Br₅?), the latter ones, however, disappearing after some time.

To avoid the formation of basic salts the solutions were mostly kept acid with pH = 1–3. Higher pH-values seemed to change the conditions for precipitation of the white crystals of CsPbBr₃ in the direction of higher CsBr-concentrations. Supersaturated solutions easily resulted so that seeding often was necessary.

Sometimes very thin needles of white crystals $\frac{1}{2}$ – 1 cm long were obtained. Apparently they grew very quickly under special conditions.

Only by hand-sorting under a microscope was it possible to obtain a pure product of white crystals—free from orange-coloured contaminations.

Under the polarizing microscope these crystals showed extinction parallel with and perpendicular to the needle-axis. When heated under the microscope on a hot stage the white crystals changed irreversibly into the orange modification at 130°C—this temperature being about 10°C lower than that mentioned by WELLS¹.

The X-ray work to be mentioned shows that the crystals have the stoichiometric composition CsPbBr₃ as found by WELLS et al¹.

Stability of the white CsPbBr₃-crystals

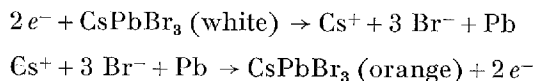
From the observation that the white needle-shaped crystals and the orange crystals could co-exist at room temperature (18–20°C) for months in aqueous solutions of CsBr with concentrations as mentioned above, it would appear that there can be only a small difference in free energy between the two forms. The white crystals eventually slowly disappeared and only orange-coloured crystals were left. With crystals of the same composition the CsBr-concentration of the solution would not be expected to influence the relative stability of the two forms, and hence it is concluded that the orange crystals are slightly more stable than the white ones. When dry, the white crystals can be kept at room temperature indefinitely.

An attempt was made to measure the difference in free energy between the two modifications. Electrochemical cells of the following type were constructed:

Pt | Pb(Hg) | CsPbBr₃(orange) | solution 27 g CsBr/100 g H₂O | CsPbBr₃(white) | Pb(Hg) | Pt.

They were kept at temperatures 19.5°C or 22.5°C. However, it was difficult to obtain reliable values for the emf.'s of the cells. Shortly after assemblage the cell had an emf. of 2–3 mv, but then drifted slowly towards lower values. Only on one occasion did the emf. stay within the interval 2.5–3.0 mv the first 24 hours after construction of the cell.

The electrode with the white CsPbBr₃-crystals was the positive electrode, suggesting the electrode processes:



Hence the white crystals are less stable than the orange ones. If a value of c. 3 mv for the emf. is accepted as being significant, the corresponding difference in free energy is $\Delta G = 3 \cdot 10^{-3} \cdot 96000 \cdot 2 \sim 600$ Joule or 140 cal/mole, which is quite small.

X-ray investigation

Oscillation and Weissenberg diagrams of single crystals of the white CsPbBr₃-compound showed that they had orthorhombic symmetry, and preliminary values for the crystal axes were determined from these photographs. Refined values were obtained from powder photographs in a Guinier type focusing camera as previously described¹, and Table 1 shows a comparison of the observed $\sin^2\theta$ -values with those calculated from the finally accepted unit cell axes:

$$a = 4.597 \pm 0.005 \text{ \AA}, \quad b = 9.72 \pm 0.01 \text{ \AA}, \quad c = 16.81 \pm 0.02 \text{ \AA}.$$

From the similarity of the powder patterns of the yellow CsPbI₃ and of the white CsPbBr₃ it is concluded that the two compounds are isomorphous with the same number of molecules in the unit cell, i. e. 4. On this basis and with the unit cell axes given above the molar volume for white CsPbBr₃ is 113.7 cc. This may be compared with the molar volume 120.5 cc for the orange modification and a value of 103.0 calculated from the molar volumes of CsBr and PbBr₂. We thus find the same trend as for the analogous iodides⁴.

⁴ C. K. MÖLLER, The Structure of Cæsium Hexahalogeno-Plumbates(II). Mat. Fys. Medd. Dan. Vid. Selsk. **32** No. 3, p. 6 (1960).

TABLE 1. Observed and calculated $\sin^2\theta$ -values for white CsPbBr₃.
CuK_α-radiation.

Indices	Estimated intensity	$10^4 \times \sin^2\theta_{\text{obs}}$	$10^4 \times \sin^2\theta_{\text{calc}}$	Indices	Estimated intensity	$10^4 \times \sin^2\theta_{\text{obs}}$	$10^4 \times \sin^2\theta_{\text{calc}}$
011	} m-w	0083	{ 0084	032	vw	0653	0651
002				123			
012	} w	0148	{ 0147	105	m	0809	0807
020				016			
013	} w	0252	{ 0252	016	vw	0820	0820
021				115			
111	} s	0364	{ 0365	124	} vw	0869	0869
112				131			
023	} w	0441	{ 0441	132	w	0932	0932
120				200			
113	} m-w	0532	{ 0533	134	w	1187	1184
121				212			
015	} m	0555	{ 0554	126	w	1294	1290
024				117			
031	} w	0589	{ 0588	213	} s	1377	1377
122				220			
	} s	0616	{ 0617	224	} vw	1716	1713
				215			

TABLE 2. Atomic parameters in white CsPbBr₃.

All the atoms are in the special positions:

$$\frac{1}{4}yz; \quad \frac{3}{4}\bar{y}\bar{z}; \quad \frac{3}{4}\frac{1}{2} - y\frac{1}{2} + z; \quad \frac{1}{4}\frac{1}{2} + y\frac{1}{2} - z$$

and for

Cs	$x = \frac{1}{4}$	$y = 0.089$	$z = 0.329$
Pb	$x = \frac{3}{4}$	$y = 0.163$	$z = 0.063$
Br'	$x = \frac{1}{4}$	$y = 0.335$	$z = 0.000$
Br''	$x = \frac{3}{4}$	$y = 0.028$	$z = 0.116$
Br'''	$x = \frac{3}{4}$	$y = 0.302$	$z = 0.211$

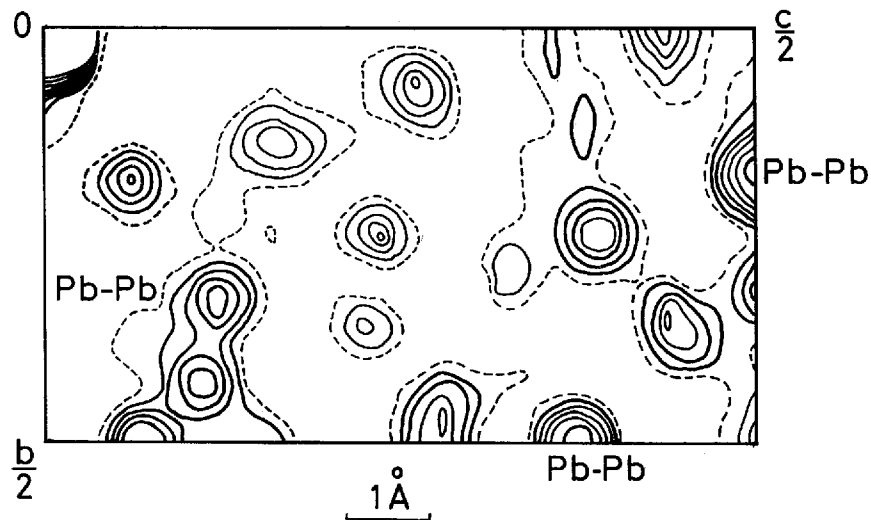


Fig. 1. Patterson projection of the white CsPbBr_3 on (100). Contours are drawn at the relative densities 0 (dashed), 25, 50, 75, 100, 150 and 200.

In order to see if there should be any relation between lattice planes in the orange and the white modifications of CsPbBr_3 , oscillation diagrams were taken of a single crystal of white CsPbBr_3 . Then the crystal was heated in a controlled flow of hot N_2 -gas and thus partly converted to the orange modification while another oscillation diagram was taken. The latter shows a powder pattern superimposed on an oscillation diagram of white CsPbBr_3 , but apparently there is no simple connection between "old" and "new" X-ray reflections, and it appears that the crystal is converted into a disordered powder of orange CsPbBr_3 within the boundary of the original crystal.

With CuK_α -radiation intensities were obtained from Weissenberg exposures by a multiple film technique as previously described¹. The crystal was rotated about the a -axis—which is also the needle axis. Its length was 0.42 mm and the cross section of the crystal $0.035 \times 0.010 \text{ mm}^2$.

Reflections of the type $h0l$ were absent for $h+1$ odd and $hk0$ were absent for k odd. No other systematic absences were observed, but $I(0kl)$ and $I(2kl)$ appeared to be equal for all values of k and l . As these rules are exactly the same as for yellow CsPbI_3 , it is inferred that the space group is also the same, no. 62 Pmnb .

The procedure and the arguments for determining the atomic arrangement from the observed intensities were from now exactly the same as described

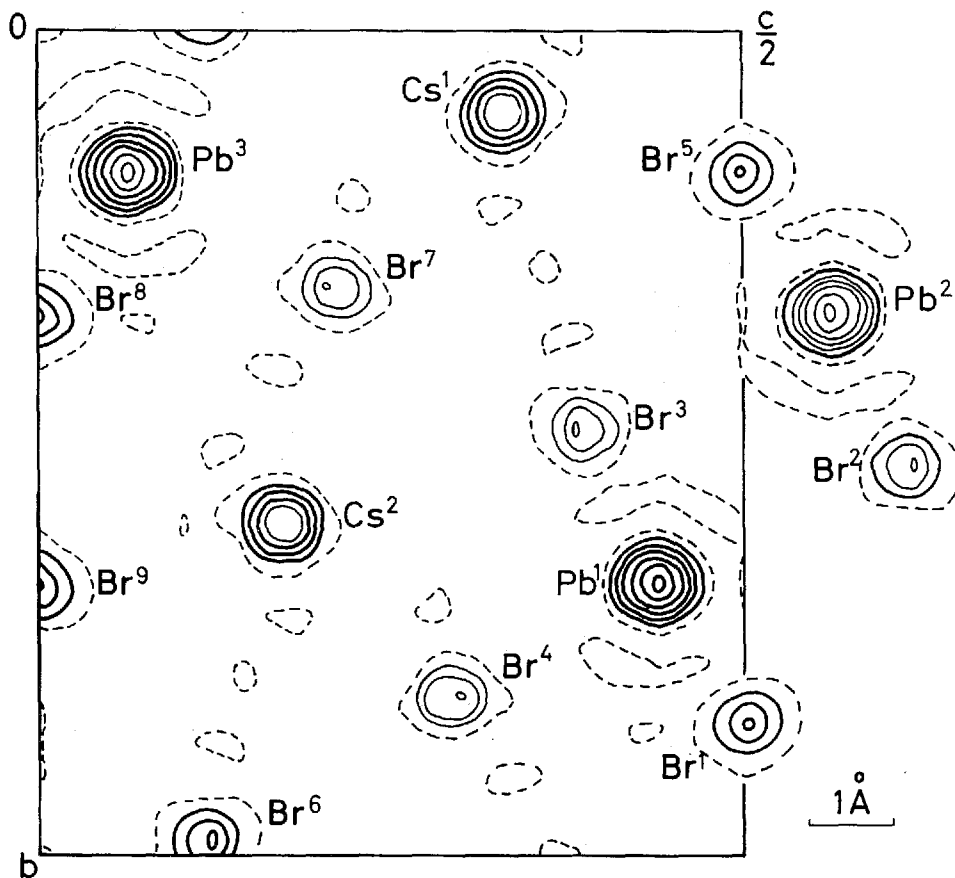


Fig. 2. Electron projection of the white CsPbBr_3 on (100). Contours are drawn at the relative densities 0 (dashed), 100, 200, 300, 400, 600 and 800.

for CsPbI_3 ¹ and no detailed account of it will be given. Suffice it to say that the structure of white CsPbBr_3 was solved independently of that of the analogous iodide and hence both Patterson and electron projections as well as difference maps were evaluated (figs. 1 and 2). The Fourier syntheses and the structure factors were calculated on a GIER electronic computer using programmes which had originally been worked out by J. DANIELSEN⁵, and atomic scattering factors from FORSYTH and WELLS' paper⁶.

⁵ J. DANIELSEN, Acta Cryst. 16 Suppl. A 171 (1963).

⁶ J. B. FORSYTH and M. WELLS, Acta Cryst. 12, 412 (1959).

TABLE 3. Comparison of calculated and observed structure factors
for white CsPbBr₃ (brought on the same relative scale).

hkl	$ F_{\text{obs}} $	F_{calc}	hkl	$ F_{\text{obs}} $	F_{calc}	hkl	$ F_{\text{obs}} $	F_{calc}
0 0 2	105	+ 85	0 2 15	46	+ 47	0 5 1	79	+ 83
0 0 4	27	- 10	0 2 19	65	- 76	0 5 2	139	+ 164
0 0 6	41	+ 31	0 2 20	23	- 32	0 5 3	74	- 74
0 0 8	144	- 129	0 2 21	10	- 12	0 5 4	108	+ 102
0 010	22	+ 10	0 3 1	22	- 19	0 5 5	77	- 69
0 012	45	+ 46	0 3 2	121	+ 147	0 5 6	58	+ 50
0 014	79	+ 65	0 3 3	84	- 79	0 5 7	12	+ 13
0 016	85	+ 102	0 3 4	128	- 137	0 5 9	122	- 128
0 018	99	+ 130	0 3 5	133	- 138	0 5 10	67	- 66
0 020	16	- 23	0 3 7	149	+ 166	0 5 11	31	+ 26
0 1 1	49	+ 54				0 5 12	65	- 58
0 1 2	85	- 85	0 3 8	31	+ 27	0 5 14	53	- 50
0 1 3	96	+ 77	0 3 9	199	+ 225	0 5 15	39	- 40
0 1 4	166	- 155	0 3 10	40	- 36	0 5 17	75	+ 76
0 1 5	201	- 227	0 3 11	70	+ 62	0 5 18	48	+ 51
0 1 6	170	- 164	0 3 12	40	+ 38	0 6 0	117	+ 133
0 1 7	118	- 94	0 3 13	43	- 39	0 6 1	97	+ 93
0 1 8	108	+ 92	0 3 15	42	- 39	0 6 2	137	+ 165
0 1 9	25	+ 21	0 3 16	41	- 48	0 6 4	68	+ 60
0 1 10	24	+ 17	0 3 17	28	- 25	0 6 6	120	- 118
0 1 11	94	- 94	0 3 19	18	+ 29	0 6 9	35	- 21
0 1 12	115	+ 119	0 3 20	21	+ 31	0 6 11	33	+ 36
0 1 13	42	- 40	0 4 0	114	- 128	0 6 12	41	- 35
0 1 14	79	+ 77	0 4 1	54	- 57			
0 1 15	57	+ 62	0 4 2	77	- 72	0 6 13	26	- 25
0 1 16	51	- 58	0 4 3	161	+ 204	0 6 14	104	+ 114
0 1 17	14	+ 17	0 4 4	47	- 42	0 6 16	84	+ 83
0 1 20	43	- 51	0 4 5	130	+ 133	0 6 18	33	+ 30
0 2 0	59	- 59	0 4 6	52	- 42	0 7 1	82	+ 83
0 2 1	87	- 104	0 4 7	68	- 67	0 7 2	75	- 77
0 2 2	63	- 66	0 4 8	115	+ 108	0 7 3	82	- 77
0 2 3	130	- 155	0 4 10	67	+ 55	0 7 6	122	- 115
0 2 4	138	- 156	0 4 11	56	- 53	0 7 7	89	- 82
0 2 5	72	- 54	0 4 12	90	- 90	0 7 9	77	- 76
0 2 6	63	+ 54	0 4 13	76	- 78	0 7 10	96	+ 95
0 2 7	149	- 148	0 4 14	39	- 34	0 7 12	71	+ 63
0 2 8	93	+ 76	0 4 15	47	- 42	0 7 17	30	+ 30
0 2 9	73	+ 58	0 4 16	50	- 44	0 8 0	92	- 87
0 2 10	12	+ 1	0 4 17	42	+ 51	0 8 1	35	+ 25
0 2 11	162	+ 181	0 4 18	33	- 37	0 8 3	48	- 45
0 2 14	104	- 117	0 4 19	23	+ 26	0 8 4	33	- 29

TABLE 3 (continued)

hkl	$ F_{\text{obs}} $	F_{calc}	hkl	$ F_{\text{obs}} $	F_{calc}	hkl	$ F_{\text{obs}} $	F_{calc}
0 8 5	131	-141	1 1 2	77	+ 76	1 3 8	28	- 21
0 8 7	24	- 7	1 1 3	153	-144	1 3 9	90	- 94
0 8 8	43	+ 37	1 1 5	43	- 33	1 3 10	91	+ 94
0 8 9	39	+ 34	1 1 6	133	+122	1 3 11	61	+ 61
0 8 11	57	+ 43	1 1 7	213	-230	1 3 12	73	+ 80
0 8 13	98	+ 97	1 1 8	123	+105	1 3 14	68	+ 70
0 8 14	33	- 35	1 1 9	160	-160	1 3 15	50	- 60
0 8 15	24	- 28	1 1 10	164	-183	1 3 16	38	+ 38
0 9 1	63	- 53	1 1 11	77	- 63	1 3 17	55	+ 74
0 9 3	20	+ 22	1 1 12	76	- 64	1 3 18	77	- 88
0 9 5	44	+ 44	1 1 14	31	+ 30	1 3 20	44	- 58
0 9 7	97	+ 92	1 1 15	38	+ 34	1 4 0	133	-176
0 9 8	64	- 65	1 1 16	19	- 27	1 4 2	130	-154
0 9 9	93	+ 90	1 1 17	40	+ 38	1 4 3	129	-146
0 9 10	80	+ 82	1 1 18	41	+ 44	1 4 4	33	- 23
0 9 14	32	- 31	1 1 19	26	+ 18	1 4 5	103	-103
010 1	59	+ 60	1 1 20	16	+ 19	1 4 6	58	- 52
010 2	96	- 90	1 1 21	41	- 80	1 4 7	74	+ 67
010 3	74	+ 66	1 2 0	87	+106	1 4 8	114	+125
010 6	57	+ 48	1 2 1	132	-204	1 4 10	92	+ 90
010 10	20	+ 19	1 2 2	200	+304	1 4 12	118	-146
011 1	23	- 21	1 2 3	91	- 91	1 4 13	77	+ 80
011 2	58	+ 46	1 2 4	63	+ 56	1 4 14	35	- 31
011 3	52	+ 47	1 2 5	31	- 20	1 4 15	30	+ 30
011 4	80	+ 79	1 2 6	158	-155	1 4 16	79	- 92
011 5	35	- 39	1 2 7	31	- 23	1 4 17	34	- 35
011 7	25	- 27	1 2 9	59	+ 52	1 4 18	53	- 65
011 10	25	- 25	1 2 10	41	- 30	1 4 19	21	- 25
012 0	67	+ 74	1 2 13	52	+ 46	1 5 1	34	- 26
012 2	43	+ 45	1 2 14	97	+117	1 5 2	100	- 99
			1 2 15	31	+ 33	1 5 3	57	- 55
1 0 1	21	- 18	1 2 16	102	+125	1 5 4	150	+178
1 0 3	103	+ 67	1 2 18	27	+ 29	1 5 5	77	+ 81
1 0 5	291	+332	1 2 19	54	- 71	1 5 7	152	+179
1 0 7	46	+ 24	1 2 20	26	+ 40	1 5 9	128	+139
1 0 9	99	- 89	1 3 1	80	+ 86	1 5 11	76	+ 77
1 0 11	76	- 69	1 3 2	141	-175	1 5 12	66	- 68
1 0 13	171	-210	1 3 3	105	-111	1 5 13	38	- 30
1 0 15	55	+ 65	1 3 4	176	-222	1 5 14	36	- 29
1 0 17	55	+ 58	1 3 5	18	- 2	1 5 15	64	- 60
1 0 21	43	+ 73	1 3 6	14	- 7	1 5 16	32	+ 42
1 1 1	98	+154	1 3 7	66	+ 64	1 6 1	111	+131

TABLE 3 (continued)

hkl	$ F_{\text{obs}} $	F_{calc}	hkl	$ F_{\text{obs}} $	F_{calc}	hkl	$ F_{\text{obs}} $	F_{calc}
1 6 2	27	+ 21	1 7 15	59	+ 64	1 9 13	21	- 24
1 6 3	79	+ 80	1 7 16	46	+ 53	1 9 14	38	+ 44
1 6 4	80	- 75	1 7 17	10	+ 6	1 10 1	24	- 24
1 6 5	74	+ 66	1 8 0	208	+ 258	1 10 2	80	- 81
1 6 7	123	+ 132	1 8 1	43	- 35	1 10 3	63	- 61
1 6 8	54	+ 48	1 8 2	60	+ 53	1 10 4	62	- 60
1 6 9	72	- 76	1 8 5	57	- 50	1 10 6	37	+ 38
1 6 11	119	- 133	1 8 8	72	- 68	1 10 7	52	- 51
1 6 13	36	- 29	1 8 12	35	+ 39	1 10 8	38	+ 38
1 6 14	66	- 62	1 8 13	48	+ 53	1 10 9	23	+ 14
1 7 1	62	- 62	1 8 14	29	+ 28	1 10 10	27	+ 19
1 7 4	94	+ 90	1 9 2	49	- 50	1 10 11	74	+ 82
1 7 5	103	- 109	1 9 3	62	+ 62	1 11 2	56	+ 55
1 7 6	85	+ 79	1 9 4	98	- 95	1 11 3	30	- 23
1 7 7	121	- 132	1 9 5	98	- 101	1 11 5	41	+ 44
1 7 8	61	- 58	1 9 6	59	- 58	1 11 7	56	+ 61
1 7 11	86	- 90	1 9 9	38	+ 35	1 11 8	29	+ 33
1 7 12	67	- 73	1 9 10	33	+ 34	1 11 9	69	+ 107
1 7 13	33	- 30	1 9 11	24	- 33	1 12 0	37	- 30
1 7 14	44	- 49	1 9 12	66	+ 68	1 12 3	56	+ 74

TABLE 4. Interatomic distances in white CsPbBr₃.

Distance	From this investigation	From Pauling's ionic radii	From Goldschmidt's radii
Pb ¹ -Br ¹	3.04 Å	3.16 Å	3.28 Å
Pb ¹ -Br ²	3.29 -		
Pb ¹ -Br ³	3.08 -		
Pb ¹ -Br ⁴	2.82 -		
Pb ¹ -Pb ²	4.46 -		
Pb-Cs	5.08 -		
Cs ¹ -Br ⁵	3.76 -	3.64 -	3.63 -
Cs ¹ -Br ¹	3.79 -		
Cs ¹ -Br ⁶	3.75 -		
Cs ¹ -Br ³	3.84 -		
Cs ¹ -Br ⁴	3.67 -		
Cs ¹ -Br ⁷	3.67 -		
Br ¹ -Br ¹	4.60 -		
Br ¹ -Br ²	4.24 -		
Br ¹ -Br ³	4.03 -		
Br ¹ -Br ⁴	4.24 -		

Structure factors which have been calculated from the atomic parameters in Table 2 are compared with the observed values in Table 3 after they have been brought on the same relative scale. Interatomic distances obtained with these parameters are given in Table 4.

Conclusion

The structure of the white CsPbBr_3 as determined from the present work is in complete analogy with that of the yellow CsPbI_3 and exhibits the same kind of irregular octahedral coordination of the halogen atoms around the lead atoms. In both structures catena-ions $(\text{PbX}_3^-)_n$ are parallel to the a -axis and the Cs-ions are held between these chain-like ions. One of the lead-halogen distances is considerably shorter than the others and also shorter than the sum of the corresponding ionic radii or Slater atomic radii: 2.82 Å against 3.16 Å or 2.95 Å, respectively. This might indicate a stronger bonding between lead and this particular halogen atom.

The variations of the interatomic distances in the two analogous crystals are also quite similar although the dispersion effects have not been considered in case of the bromide. One might, therefore, be tempted to conclude that if an uncertainty of 0.05 Å on the interatomic distances can be tolerated, the influence of dispersion may be neglected.

Acknowledgements

One of us (A.M.) is much indebted to the Carlsberg Foundation for financial support during this investigation. We are very grateful to cand. mag. E. BANG and cand. mag. B. SVEJGÅRD, lecturer in mathematics at the University of Copenhagen, for their continual help and guidance in computational matters in connection with this work.

⁷ J. C. SLATER, J. Chem. Phys. 41, 3199 (1964).